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(54) SLOW-RELEASE METAL OXIDE HOLLOW FINE PARTICLE AND ITS PRODUCTION

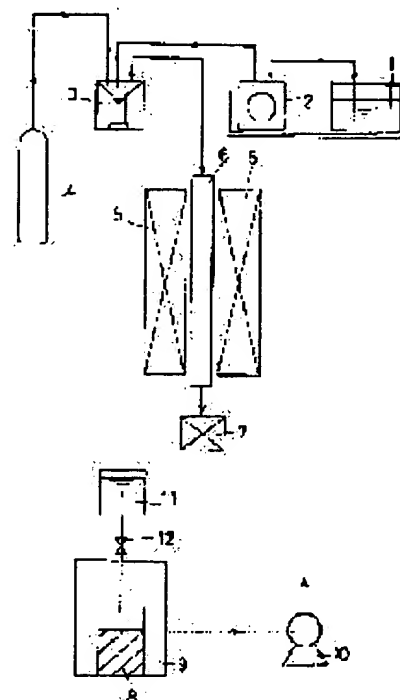
(57)Abstract:

PURPOSE: To obtain a slow-release metal oxide hollow fine particle maintaining the function of a liq. material for a long time by incorporating the liq. material into the porous part of a porous metal oxide hollow fine particle and/or into the hollow part.

CONSTITUTION: A liq. tank 1 is filled with a soln. contg. plural kinds of metallic salts, and the soln. is

continuously supplied to a raw material atomizer 3 for generating a fine liq. raw material droplet by a feed pump 2. The droplet is entrained by a carrier gas supplied from a carrier gas feeder 4 and introduced into a reaction tube 6 having a high-temp. heating element 5, the droplet is thermally decomposed in the tube 6, and a metal oxide hollow fine particle is generated in the gas-liq. mixed

phase and collected. The fine particle is then placed in a storage tank 8, a closed vessel 9 is evacuated, and the liq. material is slowly charged into a storage tank 8 from a liq. material storage tank 11. Consequently, the pressure in the fine particle is made lower than the pressure of the liq. material, and the liq. material is infiltrated into the porous part and/or hollow part.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a sustained-release metallic-oxide hollow particle and its manufacture approach. Furthermore, in detail, one kind or two or more kinds of liquefied matter is contained the porous circles of a particle, and/or in a centrum, and it is related with the manufacture approach at the sustained-release metallic-oxide hollow particle and list which carry out long duration continuation of the effectiveness which the liquefied matter has.

[0002]

[Description of the Prior Art] Generally, it is chemically [thermally / a metallic-oxide particle /, physically, and] stable, and is used in various industrial fields using engine performance, such as a photoconductivity, piezoelectric, fluorescence, and the catalyst effectiveness, for example, a zinc oxide (ZnO) particle is used for various industrial products, drugs, the vulcanization accelerator of rubber, a catalyst, a varistor (variable resistor), a coating, etc., and, recently, is used also for UV cosmetics as an ultraviolet-rays shielding material. In addition, for example, a titanium oxide (TiO₂) particle also has extensive industrial value, and, recently [, such as white pigments, abrasives, and drugs,], is used as an ultraviolet-rays shielding material. [as well as a zinc-oxide particle] Other metallic-oxide particles have various industrial value similarly.

[0003] Therefore, generally, the metallic oxide of the industrial value is very large, and in order to make the function discover to the maximum extent, porosity-izing and atomization are important for it. That is, it is because specific surface area increases very greatly, a number of a molecule of rates located in the particle front face occupied in [all / that constitutes a particle] molecularity become large, the surface energy of a particle increases porosity-izing and by atomizing, so the function is discovered very greatly. Furthermore, while putting the functional matter into the centrum by hollow-izing the fine structure of a metallic-oxide particle, the burst size of the functional matter from a particle is controllable by controlling the particle size and the aperture of a particle. As for this, the long thing to do for time amount continuation becomes possible about the effectiveness which the functional matter has, and such a new function will be given to the above-mentioned metallic-oxide particle. This will be considered to have big semantics if it thinks earnestly within saving resources and an energy-saving-visual field.

[0004] As mentioned above, it roughly divides into the quality of the material of the sustained-release particle considered to have future very important industrial value, there are an organic substance and mineral matter in it, and manufacturing methods also differ by each case. As an organic substance, there is a microcapsule formed, for example from a macromolecule polymer, and as a manufacturing method, after dissolving a physiological active substance into the buffer solution, there is a method (JP,57-112321,A) of obtaining microsphere-like sustained-release complex by producing the compound emulsion containing a vinyl polymerization nature monomer, and carrying out the polymerization of it. As other manufacturing methods, the liquid containing a water-soluble drug and the drug maintenance matter is used as an inland water layer, this is thickened thru/or solidified to specific viscosity, an

emulsification object is made by making into an oil reservoir the solution which contains a macromolecule polymerization object next, and there is a method (JP,60-100516,A) of obtaining a sustained-release microcapsule by the underwater drying method about this.

[0005] In the case of the sustained-release particle which consists of aforementioned organic substances, compared with the case of mineral matter, there is a fault of being weak, thermally, physically, and chemically. Considering the operating environment of the sustained-release particle, this is disadvantageous at the point of receiving a limit. Moreover, about a manufacturing method, since a physiological active substance, a drug, etc. which are the content ***** matter are made to live at a polymerization nature monomer and the reaction place within the liquid phase together to a sustained-release particle, it is necessary to make a polymerization reaction perform, without spoiling the activity and medicine efficiency of those content matter, and the temperature which is a polymerization reaction condition, the concentration of a polymerization nature monomer, pH, etc. have a remarkable limit. Therefore, the physical properties of the microcapsule to generate are also restricted greatly, and also when selection of the combination of a macromolecule polymer or the content matter is difficult, it is thought that it is plentifully depending on the case.

[0006] As mineral matter, in the water solution of at least one sort of inorganic compounds chosen from the inorganic-acid salt of alkali metal or the carbonate, and the halogenide of alkaline earth metal, for example The suspension and the organic solvent which made corrosion prevention or the pigment powder for antifouling paints suspend are mixed. A w/o mold emulsion and nothing, Subsequently, are the compound chosen from the ammonium salt of the halogenide of alkaline earth metal, and an inorganic acid, and the carbonate of alkali metal, and the water solution of the compound which generates water-insoluble nature precipitation by the water-solution reaction with the above-mentioned inorganic compound is mixed with the above-mentioned emulsion. There is the manufacture approach (JP,54-6251,A) of the inorganic fine particles characterized by obtaining the minute spherical porous minerals fine particles containing the above-mentioned pigment powder. In addition, there is a process (JP,57-55454,A) of the minute ball characterized by mixing the water solution and organic solvent of at least one sort of inorganic compounds which were chosen from the halogenide or nitrate of the silicate of alkali metal and alkaline earth metal, and mixing with the above-mentioned inorganic compound in the emulsion the water solution of the inorganic compound which generates water-soluble precipitation in response to a w/o mold emulsion, nothing, and a degree with the above-mentioned emulsion.

[0007] In the case of the porous particle which consists of aforementioned mineral matter, it is restricted to what contains alkali metal or alkaline earth metal as a metallic element of porous minerals fine particles on constraint of a raw material and a water-solution reaction, but since combination which does not have the reaction of the minerals fine particles and pigment must be chosen as a pigment contained to a particle and a metallic element has a limit, many cases where the selection becomes difficult arise.

[0008] As a particle which has the porous hollow structure which may serve as a sustained-release particle other than organic [above] and a non-subtlety particle on the structure of a particle For example, consist of cobalt carbonate (II) and the nearly perfect shape of a ball whose mean particle diameter is about 0.1-20 micrometers is presented. As the minute spherical porosity cobalt carbonate (II) particle characterized by having porous hollow structure and having the average pole diameter of about ten to 80 Å, and its manufacturing method there is a method (JP,55-37492,A) of carrying out the mixed reaction of the w/o mold emulsion which mixes an organic solvent with a cobalt (II) salt water solution, and is obtained, and alkali metal and (or) the hydrogencarbonate water solution of ammonium.

[0009] In the case of the aforementioned particle, the cobalt carbonate (II) particle is chemically [thermally and] unstable compared with the particle of mineral matter. For example, it is CO₂ at 350 degrees C among a vacuum. It emits, and changes to a cobalt oxide (II) particle, and they are ** and CO₂ in an acidic solution. It releases and there is a property to dissolve. Therefore, when the above-mentioned conventional technique was considered, the development of a sustained-release particle which consisted of the stable quality of the materials thermally, physically, and chemically and which is porosity and had hollow structure had become a technical problem. Moreover, development of the approach of manufacturing the particle of a wide range class cheaply continuously according to a simple

process about such a sustained-release particle as a manufacturing method was a technical problem. Then, although promising ** is carried out a metallic-oxide hollow particle in mineral matter, it consists of metallic oxides and the porous hollow particle with a sustained-release function is not yet known.

[0010]

[Means for Solving the Problem] As a sustained-release particle which consisted of the stable quality of the materials thermally [this invention persons] like the above, physically, and chemically According to the simple process of carrying out spraying pyrolysis of the solution which discovers the metallic-oxide hollow particle with porosity and hollow structure being suitable, and contains one kind or two or more kinds of metal salts After it manufactures a porous metallic-oxide hollow particle cheaply continuously and it carries out uptake, under the conditions from which this interior of a particle serves as a pressure lower than an outside By contacting one kind or two or more kinds of liquefied matter, and this particle, this liquefied matter was made to contain the porous circles of this particle, and/or in a centrum, it discovered that a sustained-release metallic-oxide hollow particle could be manufactured, research was advanced further wholeheartedly, and this invention was completed.

[0011] The summary of this invention to namely, in the porous circles of the metallic-oxide hollow particle which has (1) porosity and hollow structure, and/or in a centrum The sustained-release metallic-oxide hollow particle characterized by containing one kind or two or more kinds of liquefied matter, The solution containing one kind or two or more kinds of metal salts is made into the drop whose diameter of an average drop is 0.1-500 micrometers. a list -- (2) -- Carrier gas is used for this drop. Into a pyrogenetic-reaction furnace in the state of a vapor-liquid mixed phase Delivery, After generating the metallic-oxide hollow particle which pyrolyzes the metal salt contained in a drop inside this fission reactor, and has porosity and hollow structure, under the conditions from which this interior of a particle serves as a pressure lower than an outside By contacting one kind or two or more kinds of liquefied matter, and this particle, it is related with the manufacture approach of the sustained-release metallic-oxide hollow particle characterized by making the liquefied matter contain the porous circles of this particle, and/or in a centrum.

[0012] The metallic-oxide hollow particle used for this invention is porosity, and has hollow structure. the range whose mean particle diameter is usually 0.01-100 micrometers as a metallic-oxide hollow particle in consideration of the improvement in functional by the yield and atomization of a metallic-oxide hollow particle to generate -- the thing of the particle size of the range of 0.05-50 micrometers is mentioned preferably. Control of such a particle size can be performed by setting up suitably conditions, such as form of spraying solution concentration and raw material atomization equipment, and a weight ratio of carrier gas and metal salting in liquid. In addition, although the particle size of a metallic-oxide hollow particle can be measured by various approaches, it can be measured, for example with a scanning-type or a transmission electron microscope.

[0013] Moreover, although the average pole diameter of a metallic-oxide hollow particle has 5-desirable 1000A, 7-its 500A are still more desirable, and 10-its 100A are the most desirable. Emission of the liquefied matter is difficult, and by larger pore than 1000A, since the emission rate of the liquefied matter becomes large too much, sustained-release is not acquired from pore smaller than 5A. Although a pole diameter can be measured by various approaches, it can be measured by the porosimeter using a method of mercury penetration etc.

[0014] the time-of the percentage of hollowness of fibre of a metallic-oxide hollow particle setting the diameter of d_p and a metallic-oxide hollow particle to D_P for the diameter of the hollow globular form section -- $d_p/D_P=0.3-0.95$ -- it is 0.5-0.95 preferably. This is because the shell thickness of a metallic-oxide hollow particle is too large, it becomes difficult for the liquefied matter to pass through the interior of husks of a metallic-oxide hollow particle, the shell thickness of a metallic-oxide hollow particle is too small and a metallic-oxide hollow particle becomes easy to break, when d_p/D_P is larger than 0.95 when d_p/D_P is smaller than 0.3. It can ask for a percentage of hollowness of fibre with the electron microscope photograph of the metallic-oxide hollow particle which cut the cross section.

[0015] As a metallic oxide which has the above configurations, the oxide of metals, such as alkali metal, alkaline earth metal, and transition metals, is mentioned, for example. As an alkali metal, as Li, Na, K,

Rb, Cs, Fr, and an alkaline earth metal, specifically Be, Mg, calcium, Sr, Ba, Ra, As transition metals, Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, germanium, Ga, As of the 4th period of a periodic table, aluminum, Si, etc. are mentioned else [, such as Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn and Sb of the 5th period, and La, Hf, Ta W, Re, Os, Ir Pt Au, Hg, Tl Pb Bi of the 6th period]. As an example of a metallic oxide, MO, MO₂, M₂ O₃, etc. are mentioned, for example (it is here and M shows the above-mentioned metal). In this invention, these metallic oxides may be used independently and two or more sorts may be mixed. A zinc oxide, titanium oxide, or those mixture are suitably used from points, such as industrially useful among these metallic oxides, and a cheap thing. As the manufacture approach of such a metallic-oxide hollow particle, the approach of this invention like the after-mentioned can be used suitably.

[0016] The sustained-release metallic-oxide hollow particle of this invention is characterized by containing one kind or two or more kinds of liquefied matter the porous circles of the aforementioned metallic-oxide hollow particle, and/or in a centrum. That is, although the liquefied matter should just contain at least in either porous circles or in the centrum in this invention, it is desirable that the liquefied matter contains in both porous circles and in a centrum from the point of long-term continuation of sustained-release.

[0017] The aroma matter, a physic object, an agricultural-chemicals object, or fertilizer is mentioned, for example, without being limited especially if it is the matter which has the function which exerts a certain effectiveness on animal and plant bodies or the other body as liquefied matter used. The description which may make the above matter flow the porous circles of a metallic-oxide hollow particle [in / being liquefied here / this invention] and in a centrum is said. The aroma matter is matter which has aroma, enters from a nose and stimulates olfaction with inhalation of air, and it is divided into the natural aromatic which consists of ethereal oil (essential oil) extracted from animal and plant bodies, and synthetic perfume. As ethereal oil extracted from the animal object, various perfume, such as various synthetic perfume, such as terpenes, can be used as ethereal oil with which musk, a civet, a castor, amber grease, etc. were extracted from the plant body again. Various physic objects, such as an antiphlogistic, an antipyretic, an antihypertensive, a hypnotic drug, a nutrient, and an anticancer agent, can be used for a physic object. Various agricultural-chemicals objects, such as a herbicide and a worming agent, can be used for an agricultural-chemicals object. Various fertilizer, such as nitrogen source supply fertilizer, phosphagen supply fertilizer, and source supply fertilizer of a potassium, can be used for fertilizer. the amount of the liquefied matter contained in the sustained-release metallic-oxide hollow particle of this invention -- opening parts, such as the porous section of a metallic-oxide hollow particle, and a centrum, -- receiving -- usually -- 20 to 100 volume % -- it is 40 to 100 volume % preferably.

[0018] Next, the manufacture approach of this invention for obtaining the above sustained-release metallic-oxide hollow particle is explained to a detail, being based on a drawing. Drawing 1 is the schematic diagram showing an example of the manufacturing installation of the metallic-oxide hollow particle used suitable for this invention, and drawing 2 is a schematic diagram which is used suitable for this invention and in which showing an example of equipment which makes this particle contain the liquefied matter. In the manufacture approach of this invention, a series of processes can be performed by using the particle obtained with the equipment of drawing 1 for the equipment of drawing 2 .

[0019] The pump 2 for liquid transport is used for the solution containing one kind or two or more kinds of metal salts in a cistern 1. It sends into the coil 6 which carries out continuation supply to the raw material atomization equipment 3 which generates a minute raw material drop, is made to accompany to the carrier gas to which this raw material drop is supplied from the carrier gas feeder 4, and has the hot heating object 5. Uptake of the metallic-oxide hollow particle which was made to perform the pyrolysis reaction of a drop within a coil 6, was made to generate a metallic-oxide hollow particle in the state of a gas-solid mixed phase, and was generated within metallic-oxide hollow particle uptake equipment 7 is carried out. Next, after putting the obtained particle into the tank 8 of a metallic-oxide hollow particle and decompressing the inside of a well-closed container 9 to a predetermined pressure using a vacuum pump 10, Under the conditions to which the liquefied matter is gradually fed into the tank 8 of a

metallic-oxide hollow particle from the tank 11 of the liquefied matter, and the interior of a particle serves as a low pressure from the outside liquefied matter. Contact a particle to the liquefied matter, the liquefied matter is made to contain porous circles and/or in a centrum, and a sustained-release metallic-oxide hollow particle is manufactured. At this time, the conditions from which the interior of a particle serves as a pressure lower than the outside liquefied matter. The pressure condition that the liquefied matter permeates into the porous section inside this particle or a centrum by the differential pressure of the interior of a particle and the liquefied matter is said. As mentioned above, after decompressing the interior of a particle, after contacting both besides [to which both are contacted with atmospheric pressure etc.] an approach, the approach of pressurizing both mixed liquor a condition, the approach which combined reduced pressure and pressurization are mentioned.

[0020] What is necessary is just to be able to carry out the tank of the raw material solution to stability, although especially the cistern 1 does not limit the configuration, magnitude, and the quality of the material. Although especially the pump 2 for liquid transport is not limited, its metering pump which can carry out constant-rate supply of the raw material drop is desirable. Although atomization equipment, a two-phase flow type pressurization atomiser, etc. by supersonic vibration are mentioned as raw material atomization equipment 3, in order for the diameter distribution of a drop to obtain a very small drop narrowly, the atomization equipment by supersonic vibration is desirable. Although especially the carrier gas feeder 4 is not limited, what can supply the carrier gas of constant flow over long duration is good, and a mass type flowmeter can be used for it as the flow rate control unit, for example.

[0021] Stainless steel, the ceramics, quartz glass, etc. can be used for the quality of the material of a coil 6. Although especially the configuration of a coil is not limited, its cylindrical shape is desirable. To the direction of a tube axis, and radial, the coil as a fission reactor must be able to be made to carry out temperature control of the heating object 5 so that the isothermal section may be kept as large as possible. The range of 50-2000 degrees C is desirable, and the temperature within a reaction has the still more desirable range which is 100-1500 degrees C, and is [that what is necessary is just to set up suitably according to the class of metal salt, and the class of solvent] usually desirable. [of especially the range that is 300-1300 degrees C] It becomes [if a pyrolysis reaction rate is low and exceeds 2000 degrees C at less than 50 degrees C, rapid evaporation of a solvent will take place, and / particle diameter control] difficult and is not desirable.

[0022] Instantiation of a pyrolysis reaction mentions $\text{Ti}(\text{SO}_4)_2 \cdot \text{MgO} + \text{CO}_2 \text{ grade.} \rightarrow \text{TiO}_2 + \text{SO}_x\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_x\text{Zn}_2(\text{NO}_3) \rightarrow \text{ZnO} + \text{NO}_x\text{Ca}_2(\text{NO}_3) \rightarrow \text{CaO} + \text{NO}_x\text{MgCO}_3 \rightarrow$

[0023] Although a filter type, an electrostatic uptake type, etc. are effective in metallic-oxide hollow particle uptake equipment 7, an electrical dust precipitator or a diffusion load electrotyping electrostatic collector is desirable to long-term operation. The tank 8 of a metallic-oxide hollow particle is good in the quality of the material and the configuration of arbitration, if the tank of the particle can be carried out to stability. Glass, the ceramics, stainless steel, etc. can be used for the quality of the material. If a well-closed container 9 is the structure which can maintain the pressure inside a well-closed container at stability, it is good in the quality of the material and the configuration of arbitration. A vacuum pump 10 is stabilized and just decompresses the pressure of the well-closed container 9 interior. For example, a diaphragm-type pump, a rotary system pump, a molecular diffusion type pump, etc. can be used. As mentioned above, when making the interior of a particle contain the liquefied matter by pressurization, pressurization means, such as a high feeding pump of a discharge pressure, are used instead of a vacuum pump.

[0024] The tank 11 of the liquefied matter is good in the quality of the material and the configuration of arbitration, if the tank of the liquefied matter can be carried out to stability. in order to throw the liquefied matter into the lower part gradually to a well-closed container 9 -- the injection rate of the liquefied matter -- changing -- **** -- the inhalant canal of the liquefied matter to which the bulb 12 grade [like] was attached is attached. Moreover, when contacting the liquefied matter to a particle under pressurization, a thing with a feeding pump device (not shown) is good for a tank 11. Glass, the ceramics, stainless steel, etc. can be used for the quality of the material of the tank of the liquefied

matter.

[0025] Next, the manufacture approach of this invention using above equipment is explained. this invention -- if it is, the solution containing one kind or two or more kinds of metal salts according to the form of the aforementioned particle is used. As a class of metal salt, a hydrochloride, a sulfate, a nitrate, phosphate, a carbonate, acetate and the double salt that consists of two or more kinds of salts, the complex salt containing complex ion, etc. may be mentioned here, and either anhydrous salt or hydrate salt is OK. As an example of a metal salt Ti (SO₄)₂, and CuSO₄ and 5H₂O, Zn(NO₃)₂·6H₂O, calcium (NO₃)₂ and 4H₂O, CaCl₂, MgCO₃, Fe₃(PO₄)₂, Cu (CH₃COO)₂, and double salt -- KMgCl₃ and AlK (SO₄)₂ etc. -- as complex salt -- K₃[Fe(CN)₆] [CoCl(NH₃)₅]Cl₂ etc. -- it is mentioned. These metal salts are used with independent or mixture. When using mixture (for example, when the mixture of a titanium salt and zinc salt is used), the titanate-zinc (Zn₂TiO₄) which is the mixture or the composite of a zinc oxide and titanium oxide is obtained with pyrolysis temperature.

[0026] Water or an organic solvent can be used as a solvent of such metal salting in liquid. As an example of an organic solvent, polar solvents, such as alcohol, such as a methanol and ethanol, and N,N-dimethylformamide, dimethyl sulfoxide, hexamethylphosphoramide, are mentioned. Metal salting in liquid concentration has the desirable range of 10⁻⁵ mol/L - 20 mol/L, and its range of 10⁻⁴ mol/L - 10 mol/L is desirably good. When solution concentration is lower than 10⁻⁵mol/L, the amount of generation of the reason of a metallic-oxide hollow particle decreases extremely, and when higher than 20 mol/L, it is because the viscosity of a solution increases too much and minute drop-ization becomes difficult.

[0027] 0.1-500 micrometers, the range of the diameter of an average drop of the metal salting in liquid drop-sized is 0.1-50 micrometers, and as narrow the thing of the diameter distribution of a drop as possible is preferably desirable [a diameter] still more preferably 0.1-100 micrometers. When the diameter of an average drop is smaller than 0.1 micrometers, the particle diameter of the metallic-oxide hollow particle which generating the drop of magnitude to that extent generates when [actually difficult and] larger than 500 micrometers becomes large, and the atomization of a metallic-oxide hollow particle becomes difficult. In addition, as for the diameter of a drop, it is desirable to measure in the state of a vapor-liquid mixed phase, for example, it can measure it with a light-scattering type particle-size-distribution measuring machine.

[0028] As carrier gas, the gas which does not bar advance of inert gas or a pyrolysis reaction is used, for example, helium, air, nitrogen, etc. are used. As for the flow rate of carrier gas, it is desirable to adjust the flow rate of carrier gas so that the residence time of the carrier gas containing the raw material drop in a reaction within the pipe one may not become shorter than 1 second.

[0029] The description of the metallic-oxide hollow particle manufactured as mentioned above has porosity and hollow structure, and is a globular form-like mostly, and it is mentioned that mono dispersion nature is good. Since evaporation of a solvent and a metal salinity child's pyrolysis are mostly generated by the outside of the drop containing a metal salt in parallel to coincidence as a generation device, the husks which consist of metallic oxides generate first. Then, since evaporation of the solvent inside husks and a metal salinity child's pyrolysis happen, it is thought that a porous metallic-oxide hollow particle with the porous section or a centrum generates inside a particle. Moreover, as a source of oxygen at the time of a metallic-oxide hollow particle being formed, the intramolecular oxygen of a metal salt or the intramolecular oxygen of a solvent is used.

[0030] Next, how to contact one kind or two or more kinds of liquefied matter and this particle is explained under the conditions from which the aforementioned interior of a particle serves as a pressure lower than the outside liquefied matter. Pressurization or reduced pressure, and any are sufficient as especially the pressure in a well-closed container, without being limited. However, it is necessary to consider as the pressurization or the reduced pressure condition that the liquefied matter which has the difference of the pressure inside a metallic-oxide hollow particle and an external pressure in the outside of a metallic-oxide hollow particle can infiltrate into this interior of a particle by making differential pressure into driving force.

[0031] It is desirable to perform gradually an injection of the liquefied matter to the tank 8 of a metallic-

oxide hollow particle. That is because the powder bed of a metallic-oxide hollow particle is dispersed and effective contact of a metallic-oxide hollow particle and the liquefied matter is no longer performed, when the liquefied matter is rapidly thrown into the powder bed of a metallic-oxide hollow particle. As for the input of the liquefied matter, it is desirable to carry out to more than the volume of the powder bed of the metallic-oxide hollow particle in a tank 8. Although it is desirable to carry out beyond time amount until the liquefied matter infiltrates into the interior of a metallic-oxide hollow particle and the pressure inside a metallic-oxide hollow particle and an external pressure are balancing as for the contact time of a metallic-oxide hollow particle and the liquefied matter, when the content of the liquefied matter is good at least, contact time may be adjusted suitably.

[0032]

[Example] Hereafter, although an example and the example of a comparison explain this invention in more detail, this invention is not limited at all by these examples etc.

[0033] The zinc-oxide (ZnO) hollow particle was manufactured using the pyrolysis reactor shown in example 1 drawing 1. Zinc nitrate 6 hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and pure water are used. Prepare zinc nitrate water-solution 10-4 mol/L, and a raw material drop (5.5 micrometers of diameters of an average drop) is generated with raw material atomization equipment. The coil made from the ceramics by which temperature control was carried out to 900 degrees C using the nitrogen carrier gas controlled by 1 L/min in the flow rate (the bore of 30mm) Carried out the pyrolysis of the raw material drop to the outer diameter of 40mm, and die length of 500mm of a heating unit in delivery and the section of a reaction, the ZnO hollow particle was made to generate, and the diffusion load electrotyping electrostatic collector which attached the ZnO hollow particle obtained in the state of a gas-solid mixed phase just behind the coil outlet recovered. The crystal phase of the ZnO hollow particle obtained according to the above-mentioned conditions was amorphous, hexagonal system was intermingled in part, the mean particle diameter of a ZnO hollow particle was about 0.2 micrometers on number criteria, and 0.3 micrometers or more were [in / on 9% and 0.1-0.2 micrometers and / particle size distribution / the / in 0.1 micrometers or less / 42% and 0.2-0.3 micrometers] 7% 42%. The average pole diameter of a ZnO hollow particle was 20A, and the percentage of hollowness of fibre (= dp/DP) of a particle was 0.8.

[0034] Next, the sustained-release ZnO hollow particle of this invention containing the alpha pinene which is the aroma matter was manufactured using the equipment which makes a particle as shown in drawing 2 contain the liquefied matter. First, the 1g of the above-mentioned ZnO hollow particles is isolated preparatively to the glass beaker which is the tank of a particle, and it is left in a glass well-closed container. Then, with the vacuum pump, the inside of a well-closed container was decompressed to 10-2Torr, the alpha pinene was gradually supplied to the powder bed of a ZnO hollow particle, adjusting the cock of a separating funnel to the separating funnel which is the tank of an alpha pinene, after the injection, it was left for 20 minutes and the particle powder bed was wide opened to atmospheric air after that. In addition, at this time, the weight increment of a powder bed is 2.8g, an alpha pinene adsorbs in a ZnO hollow particle, and that weight increment is considered to have contained in the particle. As a result of using this particle as an ultrathin section with a microtome and an X-ray microanalyser's analyzing that particle cross section, it turned out that the organic substance, i.e., an alpha pinene, exists in a particle centrum and the porous section.

[0035] 1g of ZnO hollow particles containing the above-mentioned alpha pinene was put into the desiccator (capacity 1L), the 0.02 L/min style of the nitrogen gas was carried out into the desiccator, it let the gas (flow rate 0.02 L/min) discharged from a desiccator pass into the washing bottle containing a methanol (capacity 100mL), and the alpha pinenes emitted from the ZnO hollow particle were collected in the methanol. The alpha pinene concentration in the methanol which increases with the passage of time isolated methanol 1microL preparatively by the micro syringe, and measured it with the gas chromatography. Drawing 3 shows with time the alpha pinene emission concentration to the inside of a methanol for which it asked from measured value. That is, emission concentration (%/day) of the alpha pinene to the inside of the methanol per day for which it asked from the inclination of the measurement curve by the aforementioned gas chromatography is chart-ized with time amount progress. From

drawing 3, over about ten days, alpha pinene concentration was increasing gradually and, thereby, it accepted, the prolonged effect, i.e., gradual release effectiveness, of emission.

[0036] By the same approach as the above, the alpha pinene emission concentration to time amount progress was measured also in a below-mentioned example 2 and the below-mentioned example 1 of a comparison. In addition, the diameter of an average drop was measured using the light-scattering type particle-size-distribution measuring machine (a particle sizer, Japan Laser Corp. make), and the crystal phase of the generated ZnO hollow particle was measured with X-ray diffraction equipment. Moreover, the diameter of a particle was measured using the scanning electron microscope, and the average pore diameter was measured by the porosimeter (product made from POROUS MATERIALS), and it asked for the percentage of hollowness of fibre of a particle by the direct observation method by the transmission electron microscope of a particle cross section. It measured by the same approach also in the below-mentioned example 2 and the example 1 of a comparison.

[0037] The titanium oxide (TiO₂) hollow particle was manufactured using the pyrolysis reactor shown in example 2 drawing 1. Using a titanium tetrachloride and pure water, titanium-tetrachloride water-solution 10-4 mol/L is prepared, and it is TiO₂ by the same equipment and the same approach as after that and an example 1. Hollow particles were collected. TiO₂ obtained according to the above-mentioned conditions It is amorphous, the anatase mold crystal is intermingled in part, and the crystal phase of a hollow particle is TiO₂. The mean particle diameter of a hollow particle was about 0.2 micrometers on number criteria, and 0.3 micrometers or more were [in / on 10% and 0.1-0.2 micrometers and / particle size distribution / the / in 0.1 micrometers or less / 40% and 0.2-0.3 micrometers] 9% 41%. TiO₂ The average pore diameter of a hollow particle was 35A, and the percentage of hollowness of fibre (=dp/DP) of a particle was 0.8.

[0038] Next, the sustained-release TiO₂ hollow particle of this invention of an alpha pinene emission mold was manufactured by the same approach as an example 1. In addition, above TiO₂ To 1g of hollow particles, the weight increment of a powder bed is 2.9g, and, for the increment in weight, an alpha pinene is TiO₂. It adsorbs in a hollow particle and it is thought that it contained in the particle. As a result of using this particle as an ultrathin section with a microtome and an X-ray microanalyser's analyzing that particle cross section, it turned out that the organic substance, i.e., an alpha pinene, exists in a particle centrum and the porous section.

[0039] TiO₂ containing the above-mentioned alpha pinene The alpha pinene emission concentration to the inside of the methanol which increases 1g of hollow particles with the passage of time by the same approach as an example 1 was measured. The measurement result is shown in drawing 3. Like the example 1, over the long period of time, alpha pinene concentration was increasing gradually and, thereby, it accepted from drawing 3, the prolonged effect, i.e., gradual release effectiveness, of emission. However, since the average pore diameter is larger than the ZnO hollow particle of an example 1, there is more emission concentration of an alpha pinene in early stages of elapsed time than the case of an example 1, and only the part is known by that the emission concentration of an alpha pinene has become less than the case of an example 1 in the anaphase of elapsed time.

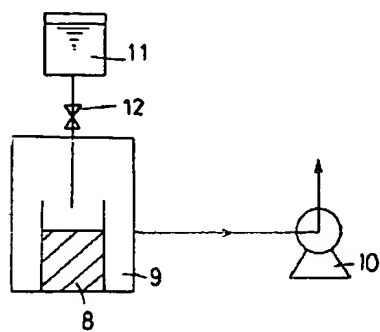

[0040] The sustained-release ZnO particle of an alpha pinene emission mold was manufactured by the same approach as examples 1 and 2 using the ZnO solid particle (based on the catalytic oxidation of the Mitsui Mining & Smelting make, a zinc steam, and air, i.e., an French method) of example of comparison 1 marketing. The crystal phase of the above-mentioned ZnO particle was amorphous, hexagonal system was intermingled in part, the mean particle diameter of the ZnO particle was about 0.2 micrometers on number criteria, and 0.3 micrometers or more were [in / on 10% and 0.1-0.2 micrometers and / particle size distribution / the / in 0.1 micrometers or less / 40% and 0.2-0.3 micrometers] 6% 44%. The scanning-type of the above-mentioned ZnO particle, and as a result of observation by the transmission electron microscope, there is no pore in the above-mentioned ZnO particle, and it did not have hollow structure. Moreover, the weight increment of a powder bed was 1g to 1g of ZnO particles. As a result of using this particle as an ultrathin section with a microtome and an X-ray microanalyser's analyzing that particle cross section, it turned out that the alpha pinene exists only in the particle front face. The alpha pinene emission concentration to the inside of the methanol which

increases 1g of ZnO particles containing the above-mentioned alpha pinene with the passage of time by the same approach as an example 1 was measured. The measurement result is shown in drawing 3 . From drawing 3 , alpha pinene emission concentration was high in early stages of elapsed time, and it almost became zero in the 6th day, and did not accept compared with examples 1 and 2, the prolonged effect, i.e., gradual release effectiveness, of emission.

[0041]

[Effect of the Invention] If the sustained-release metallic-oxide hollow particle of this invention is used, the liquefied matter can be gradually emitted from a stable metallic-oxide hollow particle thermally, physically, and chemically. As this liquefied matter, by using the aroma matter, a physic object, an agricultural-chemicals object, fertilizer, etc., it will be effective in carrying out long duration continuation of the function of this liquefied matter, and this will bring about saving resources and the effectiveness of energy saving. Moreover, according to the manufacture approach of this invention, carry out spraying pyrolysis of the solution containing a metal salt, and manufacture a porous metallic-oxide hollow particle cheaply continuously, this particle is made to contain this liquefied matter according to the simple process of manufacturing a metallic-oxide hollow particle, by the easy method of subsequently contacting this particle under this liquefied matter and a specific flow and pressure requirement, and a sustained-release metallic-oxide hollow particle can be manufactured cheaply.

[Translation done.]

Drawing selection drawing 2 

[Translation done.]